RSC | Advancing the Chemical Sciences

INEOS THE WORD FOR CHEMICALS

45th INTERNATIONAL CHEMISTRY OLYMPIAD

UK Round 1 - 2013

MARK SCHEME

Question	**1**	**2**	**3**	**4**	**5**	**Total**
Mark	**9**	**13**	**9**	**15**	**17**	**63**

Although we would encourage students to always quote answers to an appropriate number of significant figures, do not penalise students for significant figure errors. Allow where a student's answers differ slightly from the mark scheme due to the use of rounded/non-rounded data from an earlier part of the question.

For answers with missing or incorrect units, penalise 1 mark for the first occurrence in **each** question. Do not penalise for subsequent occurrences in the same question.

<table>
<tr><td colspan="4">Question 1</td></tr>
<tr><td>(a)</td><td></td><td>$3N_2H_4(l) \rightarrow 4NH_3(g) + N_2(g)$

[Ignore state symbols]</td><td>1</td></tr>
<tr><td>(b)</td><td></td><td>$\Delta_rH^\ominus = ((2 \times 46.1) + 187.8 - (2 \times 285.8) + \Delta_fH^\ominus (N_2H_4))$ kJ mol^{-1} = –241.0 kJ mol^{-1}

$\Delta_fH^\ominus (N_2H_4)$ = 50.6 kJ mol^{-1}

Decomposition enthalpy = –50.6 kJ mol^{-1}

[Positive answers of correct magnitude do not score credit.]</td><td>1</td></tr>
<tr><td>(c)</td><td>(i)</td><td>
<table>
<tr><td></td><td>N_2H_4</td><td>H_2O_2</td><td>N_2</td><td>H_2O</td></tr>
<tr><td>Ox. state of N</td><td>–2</td><td></td><td>0</td><td></td></tr>
<tr><td>Ox. state of O</td><td></td><td>–1</td><td></td><td>–2</td></tr>
</table>

[No partial credit given]</td><td>1</td></tr>
</table>

	(ii)	$CH_3OH(l) + 3H_2O_2(l) \rightarrow CO_2(g) + 5H_2O(l)$ [Ignore state symbols]	**1**
	(iii)	Amount of hydrazine = $225000\ cm^3 \times 1.021\ g\ cm^{-3} / 32.052\ g\ mol^{-1}$ = 7167 mol Amount of methanol = $862000\ cm^3 \times 0.7918\ g\ cm^{-3} / 32.042\ g\ mol^{-1}$ = 21301 mol [Both amounts needed for one mark] Heat energy evolved from hydrazine = $7167\ mol \times 622.2\ kJ\ mol^{-1}$ = 4.459×10^6 kJ Heat energy evolved from methanol = $21301\ mol \times 726.0\ kJ\ mol^{-1}$ = 15.465×10^6 kJ Total heat energy evolved from oxidation of rocket fuel = 19.9×10^6 kJ [Correct answer scores both marks. Accept -19.9×10^6 kJ]	**1** **1**
(d)	**(i)**	N_2 and H_2O [Half a mark each. Accept ‘nitrogen and water’.]	**1**
	(ii)	NO_2 [Accept ‘nitrogen dioxide’.]	**1**
(e)		$(CH_3)_2N{-}NH_2$ *This is known in the trade as UDMH (unsymmetrical dimethylhydrazine)*	**1**
		Total	**9**

Question 2			
(a)		Amount of $S_2O_3^{2-}$ = $0.0122\ dm^3 \times 0.100\ mol\ dm^{-3} = 1.22 \times 10^{-3}$ mol Amount of Cu = 1.22×10^{-2} mol Mass of Cu = $1.22 \times 10^{-2}\ mol \times 63.55\ g\ mol^{-1} = 0.775$ g Percentage of Cu by mass = 100 % × 0. 775 g / 0.800 g = 96.9 %	**1**
(b)		Volume of medal = $\pi r^2 h = \pi \times (4.25\ cm)^2 \times 0.7\ cm = 39.72\ cm^3$ Density of medal = $(0.925 \times 10.49\ g\ cm^{-3}) + (0.075 \times 8.96\ g\ cm^{-3}) = 10.38\ g\ cm^{-3}$ Mass of medal = $39.72\ cm^3 \times 10.38\ g\ cm^{-3} = 412$ g [Correct answer scores both marks.]	**1** **1**

(c)		Mass of Au = 0.067 g Amount of Ag = amount of AgCl = 6.144 g / (107.87 + 35.45) g mol^{-1} = 4.287 × 10^{-2} mol Mass of Ag = 4.287 × 10^{-2} mol × 107.87 g mol^{-1} = 4.624 g Mass of Cu = 5.000 g – 0.067 g – 4.624 g = 0.309 g Percentage of Au by mass = 100 % × 0.067 g / 5.000 g = 1.34 % Percentage of Ag by mass = 100 % × 4.624 g / 5.000 g = 92.5 % Percentage of Cu by mass = 100 % × 0.309 g / 5.000 g = 6.18 % [One mark awarded for each correct percentage. Allow error carried forward in the copper percentage. Allow minor differences due to rounding.]	**1** **1** **1**
(d)		d = tyre diameter = 0.023 m r = (wheel diameter / 2) – (tyre diameter / 2) = 0.33 m – 0.0115 m = 0.3185 m [One mark for correct value of r] volume = π^2 × 0.3185 m × $(0.023\ m)^2$ / 2 = 8.314 × 10^{-4} m^3 [Correct answer scores both marks.]	**1** **1**
(e)	**(i)**	p = 8.27 × 10^5 Pa; V = 8.31 × 10^{-4} m^3; T = 298 K $n = pV/RT$ [One mark for correct method.] n = (8.27 × 10^5 Pa × 8.31 × 10^{-4} m^3) / (8.314 J K^{-1} mol^{-1} × 298 K) n = 0.278 mol [Correct answer scores both marks; n = 0.334 mol if value of 0.001 m^3 used for volume.]	**1** **1**
	(ii)	N_2 = 28.02 g mol^{-1}; O_2 = 32.00 g mol^{-1} mass in one tyre = ((0.8 × 28.02 g mol^{-1}) + (0.2 × 32.00 g mol^{-1})) × 0.278 mol mass in one tyre = 8.011 g mass of air in both tyres = 8.011 g × 2 = 16.02 g [Mass = 19.25 g if value of 0.001 m^3 used for volume. Allow any approximations that are more accurate than this, for example if the student has decided to use 78% N_2, 21% O_2, 1% Ar.]	**1**
	(iii)	He = 4.003 g mol^{-1} mass = 2 × 0.278 mol × 4.003 g mol^{-1} mass = 2.226 g mass reduction = 16.02 g – 2.226 g mass reduction = 13.79 g [Error carried forward: accept answer from (e)(ii) minus 2.226 g or answer from (e)(ii) minus 2.674 g if 0.001 m^3 used for volume.]	**1**

		Although this mass reduction is small, it is significant enough to be considered. Unfortunately being very small, helium escapes through the rubber of tyres much more easily and so is rarely used.	
	(iv)	SF_6 = 32.06 g mol^{-1} + (6 × 19.00 g mol^{-1}) = 146.06 g mol^{-1} mass = 2 × 0.278 mol × 146.06 g mol^{-1} mass = 81.209 g mass increase = 81.209 g − 16.02 g mass increase = 65.19 g [Error carried forward: accept 81.209 g minus answer from (e)(ii), or 97.568 g minus answer from (e)(ii) if 0.001 m^3 used for volume.]	**1**
		Total	**13**

Question 3

(a)

Red	C	
Orange	G	
Yellow	G	H
Green	F	
Blue	D	H
Violet	I	

[Award half a mark for each colour. For yellow and blue both letters are needed to score the half mark for that colour.] **3**

(b)

T	lead(II) nitrate
U	sodium iodide
V	barium chloride
W	silver nitrate
X	sodium carbonate
Y	iron(II) sulfate
Z	chlorine water/dissolved chlorine gas

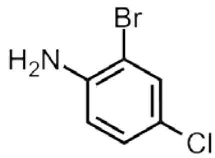
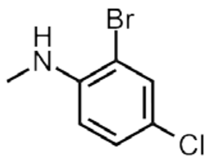
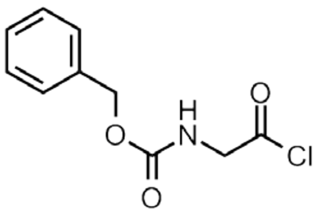
All 7 correct = 6 marks 5 or 6 correct = 5 marks 4 correct = 4 marks
3 correct = 3 marks 2 correct = 2 marks 1 correct = 1 mark

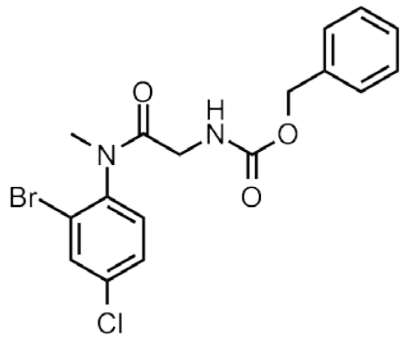
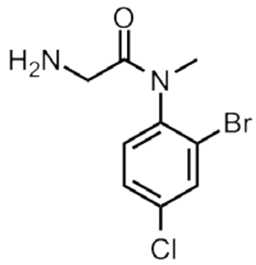
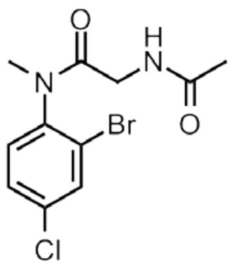
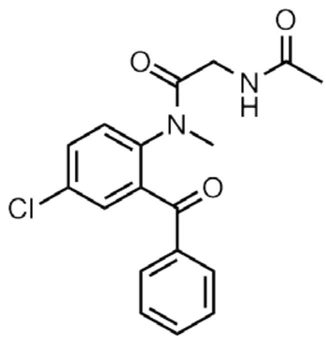
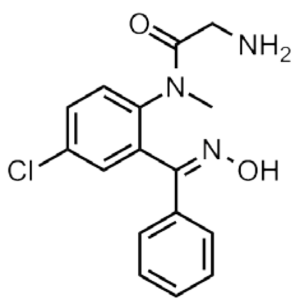
[Ignore spelling errors as long as substance is recognisable. Oxidation states not needed. Accept if correct chemical formulae have been written instead of words.] **6**

Total 9

Question 4

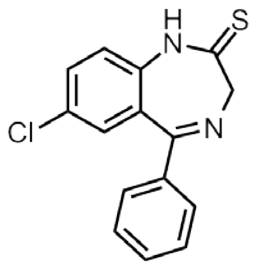
(a)	**(i)**	10.8 % *More modern syntheses have considerably improved upon this overall yield.*	**1**

	(ii)	Mass of diazepam per dose = 5×10^{-3} g Total mass of diazepam = 5×10^{-3} g × 4 × 365 × 3 Total mass of diazepam = 21.9 g [Allow an extra day added for a leap year.] Amount of diazepam = 21.9 g / 284.734 g mol^{-1} Amount of diazepam = 0.0769 mol Amount of 4-chloroaniline = 0.0769 mol / 0.108 Amount of 4-chloroaniline = 0.712 mol Molecular formula of 4-chloroaniline = C_6H_6NCl M_r of 4-chloroaniline = (6 × 12.01 g mol^{-1}) + (6 × 1.008 g mol^{-1}) + 35.45 g mol^{-1} + 14.01 g mol^{-1} M_r of 4-chloroaniline = 127.568 g mol^{-1} Mass of 4-chloroaniline = 0.712 mol × 127.568 g mol^{-1} Mass of 4-chloroaniline = 90.8 g [Correct answer scores both marks. Error carried forward: accept answers based on incorrect answer to (a)(i)]	1 1
(b)		Structure of **A**  [If bromine atom is in wrong position on benzene ring, no credit is given here, but full credit is awarded in B, D, E and F provided rest of structure correct.]	1
		Structure of **B**  	1
		Structure of **C**  	1

	Structure of **D** 	**1**
	Structure of **E** 	**1**
	Structure of **F** 	**1**
	Structure of **G** 	**1**
	Structure of **H**  [Allow stereoisomer with other geometry around C=N bond.]	**1**

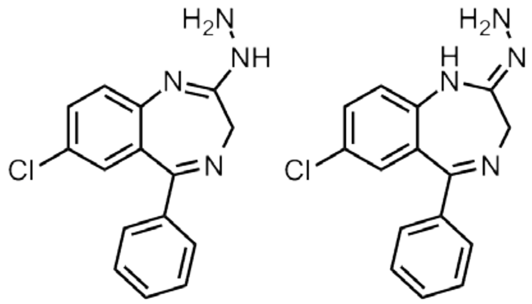
(c)

Structure of **I**



1

Structure of **J**

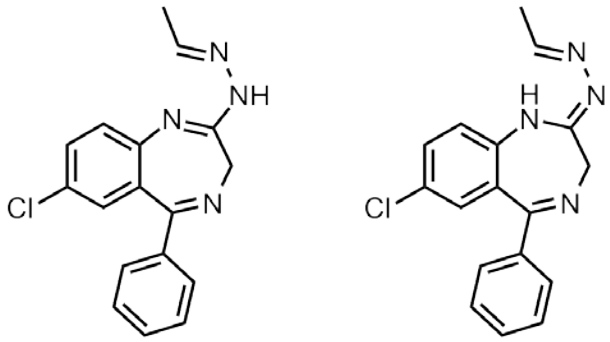


[Accept either structure. Also allow stereoisomer with other geometry around the top C=N bond in the right hand structure.]

The left structure is believed to be the predominant one.

1

Structure of **K**



[Accept either structure and also any stereoisomers with alternative geometries around C=N bonds not in the ring.]

The left structure is believed to be the predominant one.

1

(d)

Isomerisation	Hydrolysis	Condensation	Oxidation	Reduction
			✓	

DEAD is also sometimes known as DEADCAT.

1

Total	**15**

Question 5

(a)		$C_4H_9N_3O_2.H_2O$ or $C_4H_{11}N_3O_3$ [Accept answers where order of elements is different.]	**1**

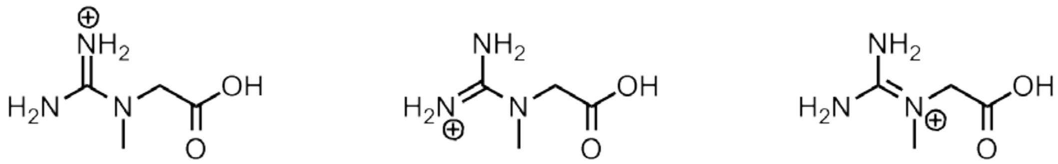
(b)

Carbon Atom in Creatine	Carbon Atom in Amino Acid
1	**H**
2	**C**
3	**A**
4	**B**

All four correct = 3 marks Three correct = 2 marks Two correct = 1 mark

3

(c) (i)

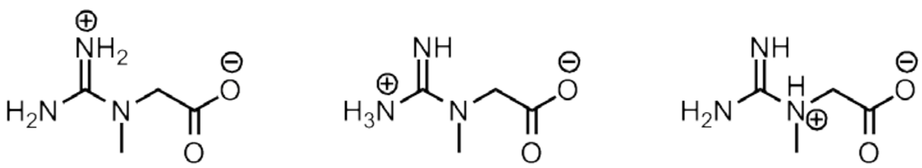


[Any one of the three resonance structures shown above is worth 2 marks i.e. the extra proton must be on the uppermost nitrogen as drawn in the diagram for 2 marks. Either of the two structures shown below should be awarded 1 mark.]

The uppermost nitrogen is protonated as this maintains the delocalisation present in the neutral guanidinium group in the conjugate base form.

2

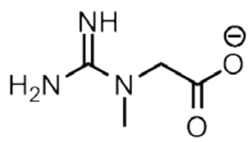
(ii)



[The first structure is chemically correct, but any one of the three structures shown above is worth 1 mark. – The mark for protonating the correct nitrogen is awarded in part (i). Allow the other two resonance forms for the guanidinium group in the structure on the left as in part (i)]

1

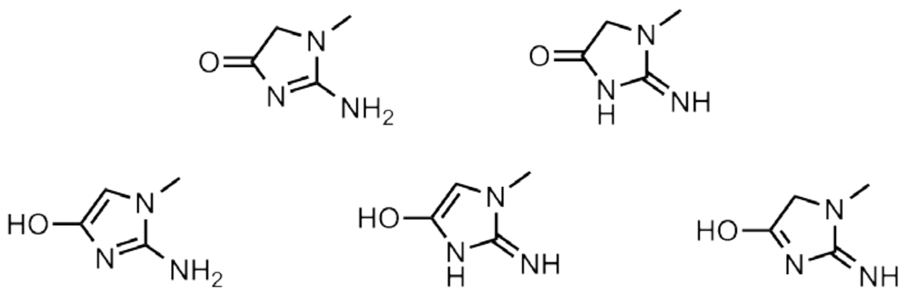
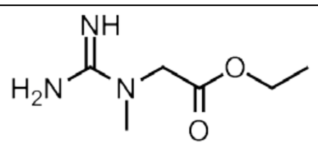
(iii)



1

(d)

Carbon atom	Singlet	1:1 doublet	1:2:1 triplet	1:3:3:1 quartet	1:4:6:4:1 quintet	No signal observed	Marks
C	✓						**1**
D			✓				**1**
F			✓				**1**

(e)		**E** and **K** [Award half a mark each. If other letters are written minus half a mark for each other letter down to zero.]	**1**
(f)		[Any one of the five alternatives below is to be awarded the mark.] *The percentage of each tautomer is solvent dependent, although the top two are by far the most important. In protic solvents, hydrogen-bonding favours the top left structure.* 	**1**
(g)		K = [Creatinine] / [Creatine] K = Integral height of signal A / Integral height of signal B K = 4 [This has no units. Award values between 3.5 and 5.0 the mark. There must be evidence of working/using the correct integral method to gain the mark.] *Creatinine is favoured at more acidic pHs and creatine at more alkaline pHs.*	**1**
(h)		 [The correct structure is to be awarded 3 marks. The hydrochloride salt of this molecule (protonated on any one nitrogen) should also be awarded 3 marks. Incorrect structures may score 2 marks if they obey any two of the three criteria below, and 1 mark for obeying any one of the criteria.] ■ A total of 10 C–H protons in the molecule. *This shows the student has successfully used the integrals in the spectrum to calculate the number of hydrogens.* ■ The presence of a discrete ethyl group in the molecule. *This shows the student has understood the coupling patterns in the NMR.* ■ The presence of an ester functional group in place of the carboxylic acid. *This shows the student has understood the ionisation states of the molecule at different pHs.*	**3**
		Total	**17**